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(54) IMPROVEMENTS IN OR RELATING TO LUMINESCENT MATERIALS

(71) We, THE GENERAL ELECTRIC COMPANY LIMITED, of 1 Stanhope Gate, London W1A 1EH, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to luminescent materials of the type consisting of crystalline inorganic material activated so as to be excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å, and by cathode rays, and is an improvement in or modification of the invention claimed in Claim 1 of Patent Specification No. 1,087,655. The invention is also concerned with a method of manufacturing the luminescent material described, and with electrical devices incorporating such material.

The luminescent material claimed in Claim 1 of Patent Specification No. 1,087.655 is composed of the elements silicon, oxygen, one or more of the alkaline earth metals calcium, strontium and barium, one or both of the halogens fluorine and chlorine, and europium in the divalent state, the proportion of europium being in the range of 0.5% to 20% by weight of the material, and the material being activated by the europium present so as to be excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å, and by cathode rays.

According to the present invention, a crystalline inorganic luminescent material which is an improvement in or modification of the luminescent material claimed in Claim 1 of Patent Specification No. 1,087,655 consists of a calcium chlorosilicate having substantially the composition represented by the formula $Ca_2SiO_4.CaCl_2$, activated by europium in the divalent state so as to be excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å and by cathode rays, the proportion of europium present being in the range of 0.001 mole percent to 0.1 mole percent of the calcium chlorosilicate.

The europium content of the material is preferably in the range of 0.01 mole percent to 0.05 mole percent of the calcium chlorosilicate.

The luminescent material of the present invention is characterised by a crystal structure as described in the article "Die Kristalstruktur von Tricalciummonosilikatdichlorid —$Ca_2SiO_4.CaCl_2$" by Von Reinhard Czaya and Gertrud Bissert, published in the journal "Acta Crystallographica", volume B27, page 747 (1971). This crystal structure is different from that characteristic of the europium activated strontium chlorosilicate material described in Patent Specification No. 1,087,655.

The calcium chlorosilicate material of the invention is excited by long and short wavelength ultra violet radiation, and by cathode rays, to exhibit green luminescence, with a peak in the brightness of the emission at wavelengths in the regions of 5150 Å. This emission thus occurs at longer wavelengths than that of a known luminescent material consisting of calcium silicate activated by divalent europium. The efficiency of luminescence of the calcium chlorosilicate material is high, and the temperature persistence of the emission is good, so that the material is suitable for use in devices operating at elevated temperatures, up to about 300°C. In addition, the development of emission on excitation, and the decay of the emission on removal of the excitation, both take place rapidly: these properties are advantageous for some applications for which the luminescent material is suitable.

The luminescent material of the invention is manufactured by heating a mixture consisting of the constituents of said material, and/or of compounds which react to produce such constituents during the heating, said mixture preferably including a proportion of calcium chloride in excess of that

required to be incorporated in the final product, to function as a flux, the heating being continued for a period of at least three hours at a temperature of at least 600°C, to effect reaction of the said mixture to produce europium-containing calcium chloro-silicate, and at least a part of the heating process being carried out in a neutral or reducing atmosphere, to ensure that the europium is present in the divalent state in the final product. The product of the heating is washed with water to remove the excess calcium chloride if present. If desired the starting mixture may consist of compounds which react together during the heating to form calcium silicate, together with europium oxide and calcium chloride.

However, in the preferred method of manufacturing the material, europium-activated calcium silicate is preformed by any known method, for example by firing a mixture of calcium carbonate, silica and europium oxide, in appropriate relative proportions, at a temperature in the range of 800°C to 1250°C, and is converted to europium-activated calcium chlorosilicate by heating with hydrated calcium chloride, $CaCl_2.2H_2O$, in an amount up to 10 moles excess over that required in the final product, the heating being carried out at a temperature in the range of 600°C to 900°C for at least three hours. If these steps, and the washing step if required, have been carried out in air or other oxidising atmosphere, the product is then heated in a reducing atmosphere, suitably a mixture of hydrogen and nitrogen containing 5% to 20% of hydrogen, by volume, at a temperature in the range of 600° to 900°C for 1 to 2 hours, to reduce the europium to the divalent state. However, if the steps of preparing the europium activated calcium silicate and heating with calcium chloride are carried out in a reducing or neutral atmosphere, a subsequent reducing heat treatment may not be necessary.

A specific method which we have carried out for the preparation of a luminescent material in accordance with the invention will now be described in the following example.

Calcium silicate containing europium was first prepared by mixing calcium carbonate, silica and europium oxide powders, in the proportions of 9.5 grams $CaCO_3$, 3.25 grams SiO_2 and 0.36 gram Eu_2O_3, firing the dry mixture for one hour at 900°C in air, regrinding, and refiring for 3 hours at 1250°C in air.

2 grams of the product of the above procedure were mixed with 10 grams of hydrated calcium chloride, $CaCl_2.2H_2O$, and the mixture was fired for 4 hours at 800°C in air. The material so produced was ground and washed with distilled water to remove the excess calcium chloride, then dried and fired for 1½ hours at 750°C in a flowing atmosphere consisting of 20% hydrogen and 80% nitrogen, by volume.

The final product, which had the composition $Ca_2SiO_4.CaCl_2$—$0.05Eu^{2+}$, had a nearly white body colour, and exhibited green luminescence under excitation by ultra violet radiation of wavelengths 2537 Å and 3650 Å and by cathode rays.

WHAT WE CLAIM IS:—

1. A crystalline inorganic lumiescent material which is an improvement in or modification of the luminescent material claimed in Claim 1 of Patent Specification No. 1.087,655, and which consists of a calcium chlorosilicate having substantially the composition represented by the formula $Ca_2SiO_4.CaCl_2$, activated by europium in the divalent state so as to excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å and by cathode rays, the proportion of europium present being in the range of 0.001 mole percent to 0.1 mole percent of the calcium chlorosilicate.

2. A luminescent material according to Claim 1, wherein the europium content is in the range of 0.01 mole percent to 0.05 mole percent of the calcium chlorosilicate.

3. A method of manufacturing a luminescent material according to Claim 1 or 2, which comprises heating a mixture consisting of the constituents of said material, and/or of compounds which react to produce such constituents during the heating, the heating being continued for a period of at least three hours at a temperature of at least 600°C to effect reaction of the said mixture to produce europium-containing calcium chlorosilicate, and at least a part of the heating process being carried out in a neutral or reducing atmosphere.

4. A method according to Claim 3, wherein the said mixture consists of compounds which react together to form calcium silicate, together with europium oxide and calcium chloride.

5. A method according to Claim 3 or 4, wherein the said mixture includes a proportion of calcium chloride in excess of that required to be incorporated in the final product, and the said excess is subsequently removed by washing the product of the heating with water.

6. A method according to Claim 3, wherein the said mixture consists of preformed europium-activated calcium silicate and hydrated calcium chloride, $CaCl_2.2H_2O$, in a proportion up to 10 moles excess over that required in the final product, and wherein the heating is carried out at a temperature in the range of 600°C to 900°C for at least three hours.

7. A method according to Claim 6.

wherein the europium-activated calcium silicate is produced by heating a mixture of calcium carbonate, silica and europium oxide, in the requisite relative proportions, at a temperature in the range of 800°C to 1250°C.

8. A method according to Claim 6 or 7, wherein the steps of preparing the europium-activated calcium silicate and heating the latter with calcium chloride, are carried out in an oxidising atmosphere, and the product is then heated in a reducing atmosphere for one to two hours at a temperature in the range of 600°C to 900°C.

9. A method of manufacturing a luminescent material according to Claim 1, carried out substantially as hereinbefore described in the specific example.

10. A luminescent material manufactured by the method according to Claim 9.

11. An electrical device incorporating a luminescent material according to Claim 1, 2 or 10, the said material being so disposed and the device being so arranged that the material is excited to luminescene during operation of the device.

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